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Energy-induced curable compositions

A polymerizable composition comprises a polymeric, preferably soluble, first free group, consisting of at least one ethylenically-unsaturated monomer (2) at least one quaternary ammonium salt and a curable agent comprising an organometallic compound and an anionic salt.

ENERGY-INDUCED CURABLE COMPOSITIONS

Field of the Invention

This invention relates to an energy-polymerizable composition comprising an ethylenically-unsaturated monomer, an epoxy monomer, or polyurethane precursor, and as curing agent a combination of an organometallic compound and an oxidizing agent and a method thereof. In another aspect, cured articles comprising the composition of the invention are disclosed. The compositions are useful, for example, as protective coatings, binders for magnetic media or abrasives, adhesives, and in graphic arts applications.

Background Of The Invention

Various polymeric coatings and articles are produced in processes involving the use of organic solvents. There is an intense effort by law, researchers, and industry to promote high and 100% solids formulations to reduce or eliminate the use of such solvents and the attendant costs and environmental contamination. These processes require a latent catalyst or latent reaction promoter which can be activated in a controlled fashion.

Thermal curing of polyurethane precursors using reaction promoters such as tin salts and tertiary amines is known in the art. Curing of polymerizable mixtures of polyacrylates with polyols (referred to as polyurethane precursors) using thermally latent catalysts is known in the art (see for example U.S. Patent Nos. 4,521,545, and 4,582,881).

Photocuring of urethane (meth)acrylates is well known (see T. A. Speckhard, K.K.S. Huang, S.B. Lin, S.Y. Tsay, M. Kozlowski, Y.S. Ding, S.L. Cooper, J. Appl. Polymer Science, 1985, 30, 847-868; C. Blumstein, Polym. Prepr. Technol. Eng. 1987, 17, 83-88; Photocuring of polyurethane precursors using diazonium salts, tertiary amine precursors, and organotin compounds is also known (see U.S. Patent Nos. 4,544,468, 4,549,945, and EP 28,698, Derwent abstract). All of these methods suffer from one or more of the following disadvantages: sensitivity to oxygen, requirement of ultraviolet and/or high intensity light, the need for modified resins, loss or dilution of urethane properties, low activity, poor solubility, and poor pot-life.

The prior art discloses processes for the polymerization of epoxy materials. It is further known that a metalocene, such as ferrocene, can be used as a curing accelerator for epoxy materials (U.S. Patent No. 3,705,129; U.S. Patent Nos. 3,710,881, 3,714,008, 3,887,364 and 4,237,242 relate to the use of transition metal complexes in the reaction between polyepoxide and polyfunctional curing additives, but they do not teach the polymerization of epoxide group-containing compositions not containing a curing additive. The polymerization of epoxide group-containing materials is also known. Among such processes are those in which the polymerization catalyst is a radiation-sensitive organotin salt of a Lewis acid (e.g. diazonium salts as described in U.S. Patent No. 3,794,578 and U.S. Patent No. 4,080,274; hafnium salts as disclosed in U.S. Patent No. 4,028,705; and the organotin salts of Group VA elements, particularly the antimony salts, as disclosed in U.S. Patent No. 4,058,400, or a dicarbonyl chelate compound of a Group IIIA-VA element as disclosed in U.S. Patent No. 4,088,081). These compositions are limited to ultraviolet radiation for polymerization. Furthermore, the dicarbonyl chelates are moisture sensitive.

U.S. Patent No. 4,210,388 teaches the thermal curing of cationically polymerizable compositions using crown salts and reducing agents.

Energy polymerizable compositions comprising ionic salts of organometallic complex cations and cationically sensitive materials and the curing thereof has been taught (see European Patent No. 09,851, 1984 094,914 1803 Derwent abstract, and 094,915, 1983, Derwent abstract).

Neutral organometallic compounds have been used in combination with neutral halogenated compounds for the photocuring of ethylenically-unsaturated monomers (J. Smets, Pure G. Appl. Chem., 53,611,615 (1981); H.M. Wagner, M.D. Putnick, J. Photogr. Sci. 29, 230-236 (1981)).

The use of certain photoinitiators with crown salts for initiation of polymerization of ethylenically-unsaturated monomers is also well known in the art. This technique has found applications in printing, duplicating, copying, and other imaging systems (see J. Koser in Light Sensitive Systems: Chemistry and Application of Nonlinear Media Photographic Processes, Wiley, New York, 1985, pp 159-163). Arylodonium salts have been previously described for use as photoinitiators in addition-polymerizable compositions. (See

U.S. Patent Nos. 3,728,313, 3,741,768, 3,893,008, 4,228,232, 4,288,083 and 4,488,887; H. J. Trops and H. Baumann, Wiss. Z. Tech. Hochschule Leuna-Merseburg, 28, 439 (1984); H. Baumann, B. Schenke, H. J. Trops and U. Lammert, J. Prakt. Chem., 359 (1985), 215 (1985); and H. Baumann, U. Grosse and H. J. Trops, Ber. Polym. J., 22 (4), 315 (April 3, 1985).

Summary of the Invention

Briefly, the present invention provides an energy polymerizable composition comprising 1) at least one ethylenically-unsaturated monomer, or 2) at least one epoxy monomer, or 3) polyurethane precursor, and as curing agent a combination of an organometallic compound and an oxidizing agent. The compositions are useful as protective and decorative coatings, waxes, adhesives, in restorative and denture applications, and in imaging applications.

What is not taught in the prior art, but what is taught in the invention, is the use of organometallic compounds in combination with crown salts for the photo- and electron beam-induced curing of ethylenically-unsaturated monomers, epoxy monomers or polyurethane precursors, and the curing of ethylenically-unsaturated monomers or polyurethane precursors.

Advantages of compositions of the present invention when utilized as 100% reactive coating compositions include:

An industrial process invention is disclosed that will reduce, eliminate, or eliminate the generation of industrial solvent waste while reducing energy consumption.

Radiation processing, particularly utilizing electron beam and photogenerated catalysts, has potential capability for penetrating and polymerizing thick and pigmented coatings.

More readily available monomers can be used in place of functionalized oligomers based on the prior art thereby resulting in lower viscosity monomer solutions which are easier to coat than more viscous oligomer solutions.

Expanding the scope of curable monomers to include polyacrylates-polyols and epoxides allows increased flexibility in designing coatings with specific properties.

In this application:

"energy-induced curing" means curing by means of electromagnetic radiation (ultraviolet and visible) scattered particles (including electron beam), and thermal (infrared and heat) means.

"ethylenically-unsaturated monomer" means those monomers that polymerize by a free-radical mechanism "catalytically-effective amount" means a quantity sufficient to effect polymerization of the curable composition to a polymerized product at least to a degree to cause an increase in the viscosity of the composition.

"organometallic compound" means a chemical substance in which at least one carbon atom of an organic group is bonded to a metal atom ("Basic Inorganic Chemistry", F.A. Cotton, G. Wilkinson, Wiley, New York 1978, p. 487).

"polyurethane precursor" means a mixture of one or more monomers of the type including diisocyanates and polyacrylates, and one or more monomers of the type including diols and polyols, and bearing at least two isocyanate-reactive hydrogen atoms may be substituted by diols and polyols (also bearing at least two isocyanate-reactive hydrogen atoms) in a 1:2 to 2:1 ratio.

"bridging ligand" means a ligand that binds to two or more metals in the presence or absence of metal-metal bonds.

"polyacrylates" means an aliphatic or aromatic acrylate bearing 2 or more acrylate groups.

"polyol" means an aliphatic or aromatic compound containing 2 or more hydroxyl groups, and

"crown salt" means salts of cationic compounds such as cesonium, hafnium, and hypervalent Group VA elements.

Detailed Disclosure of the Invention

The present invention provides, in a preferred embodiment, a photopolymerizable composition comprising at least one ethylenically-unsaturated monomer, or at least one epoxy monomer, or polyurethane precursor, and a two-component curing agent. Therefore, and in a second embodiment, a thermally polymerizable composition comprising at least one ethylenically-unsaturated monomer or polyurethane precursor and a two-component curing agent. Therefore, the curing agent in all cases comprising

- $\text{Ru}(\text{CO})_2(\text{10-phenanthroline})$
 $\text{Ru}(\text{CO})_2(\text{10-phenanthroline})$
 $\text{Ru}(\text{CO})_2(\text{2,2'-biquinoline})$
 $\text{Ru}(\text{CO})_2$
 $\text{Os}(\text{CO})_2$
 $\text{Ru}(\text{CO})_2(\text{PPh}_3)_2$
 $\text{Ru}(\text{CO})_2(\text{Ph}_3\text{P-CH}_2\text{CH}_2\text{PPh}_3)$
 $\text{Fe}_2\text{Ru}(\text{CO})_2$
 $\text{Ir}_2(\text{CO})_2$
 $[\text{Co}(\text{H}_2\text{CO})_2]$
 $\text{CoFe}(\text{CO})_2(\text{CH}_3)_2\text{Ph}$
 $\text{CoFe}(\text{CO})_2(\text{COPh})$
 $\text{CoFe}(\text{CO})_2(\text{SiPh}_3)$
 $[\text{Co}^+ \text{Fe}(\text{CO})_2]$
 $\text{Co}(\text{CO})_2\text{Fe-Fe}(\text{CO})_2\text{PPh}_3/\text{Co}$
 $(\text{Me}_2\text{SCo})\text{PPh}_3$
 $\text{Co}(\text{CO})_2\text{Me-Me}(\text{CO})_2\text{PPh}_3/\text{Co}$
 wherein

Me is methyl

Ph is phenyl

Co is cis^2 -cyclopentadienyl

Co⁺ is cis^2 -pentamethylcyclopentadienyl

A wide variety of monomers can be energy polymerized using the curing agent of the invention. Suitable compounds containing at least one ethylenically-unsaturated double bond, can be monomers and/or oligomers such as (meth)acrylates, (meth)acrylamides, and vinyl compounds, and are capable of undergoing addition polymerization. Such monomers include mono-, di-, or polyacrylates and methacrylates such as methyl acrylate, methyl methacrylate, ethyl acrylate, isopropyl methacrylate, n-butyl acrylate, styryl acrylate, allyl acrylate, glycidyl acrylate, glycidyl methacrylate, ethylene glycol dimethacrylate, 1,3-propanediol dimethacrylate, trimethylolpropane triacrylate, 1,2,4-butanetriol triacrylate, 1,4-cyclohexanediol diacrylate, pentaerythritol tetraacrylate, pentaerythritol tetramethacrylate, sorbitol triacrylate, bis[1-(2-acryloyloxyethyl)-2-methylpropane] dimethacrylate, bis[1-(2-acryloyl-3-hydroxyethyl)-2-methylpropane] dimethacrylate, bis-hydroxyethylmethacrylate dimethacrylate, the triacrylates and tetraacrylates of polyethylene glycols of molecular weight 200-600, copolymerizable mixtures of acrylated monomers such as those of U.S. Patent No. 4,682,274, and acrylated oligomers such as those of U.S. Patent No. 4,642,128, unsaturated amides such as acrylamide, methylene bis-acrylamide, methylene bis-methacrylamide, 1,3-bis(methacryloyl)-2-methylpropane triacrylamide, diallylamine bis-acrylamide and bis-methacrylamide, methacrylates, and vinyl compounds such as styrene, diethyleneglycol diethyl phthalate, divinyl succinate, divinyl adipate, divinyl phthalate, and vinyl acetate as disclosed in U.S. Patent NO. 4,304,705. Mixtures of two or more monomers can be used if desired.

The polyacrylates component of the polyurethane prepolymers that can be cured or polymerized in the dual curing systems of the present invention may be any olefinic, cycloolefinic, acyclic, aromatic, or heterocyclic polyacrylates, or any combination of such polyacrylates. Particularly suitable polyacrylates correspond to the formula



in which p is an integer 2 to 4, and Q represents an olefinic hydrocarbon di-, tri-, or tetra-ethyl containing from 2 to 100 carbon atoms, and zero to 80 heteroatoms, a cycloolefinic hydrocarbon radical containing from 4 to 100 carbon atoms and zero to 80 heteroatoms, an aromatic hydrocarbon radical or heterocyclic aromatic radical containing from 5 to 15 carbon atoms and zero to 15 heteroatoms, or an arylidene hydrocarbon radical containing from 6 to 100 carbon atoms and zero to 80 heteroatoms. The heteroatoms that can be present in Q include non-permanent oxygen, sulfur, non-aromatic nitrogen, halogen, silicon, and non-functional phosphorus.

Examples of polyacrylates are as follows: ethylene diacrylate, 1,4-hexamethylene diacrylate, 1,6-hexamethylene diacrylate, bis(methyl hexamethylene diacrylate), 1,15-dodecane diacrylate,

cyclobutene-1,3-diacrylate, cyclobutene-1,3- and -1,4-diacrylate and mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-6-oxocyclohexenyl cyclohexane (see German Auslegeschrift No. 1,262,788, U.S. Patent No. 3,401,180), 2,4- and 2,6-hexamethylene diacrylates and mixtures of these isomers, hexafluoro-1,3- and/or -1,4-phenylene diacrylates, pentafluoro-2,4- and/or -4,4'-diphenylene diacrylates, 1,3- and 1,4-phenylene diacrylates, 2,4- and 2,6-xylylene diacrylates and mixtures of these isomers, diphenylmethane-2,4- and/or -4,4'-diacrylates, hexafluoro-1,3-diacrylates and the reaction products of four equivalents of the aforementioned acrylate-containing compounds with compounds containing two isocyanate-reactive groups.

According to the present invention, it is also possible for example, to use isopropyl methacrylate-4,4'-diacrylate, polyphenyl polyethylene polyacrylates described in British Patent Nos. 874,489 and 848,871, m- and p-oxycyclohexenyl sulfonyl isocyanates according to U.S. Patent No. 3,404,088, perchlorinated aryl polyacrylates of the type described, for example, in German Auslegeschrift No. 1,167,801 (U.S. Pat. No. 3,277,138), polyacrylates containing carbamate groups of the type described in U.S. Patent No. 3,162,165 and in German Offenlegungsschrift Nos. 2,894,468, 2,957,889 and 2,982,380, norbornene diacrylates according to U.S. Patent No. 3,498,338, polyacrylates containing carbamate groups of the type described, for example, in British Patent No. 894,888, in German Pat. No. 791,100, Dutch Patent Application No. 7,162,824, polyacrylates containing isocyanate groups of the type described, for example in U.S. Patent No. 3,091,873, in German Patent No. 1,882,788, 1,252,687 and 1,087,384 and German Offenlegungsschrift Nos. 1,928,804 and 2,894,048, polyacrylates containing urethane groups of the type described, for example, in British Patent No. 782,289 or in U.S. Patent Nos. 3,394,164 and 3,644,467, polyacrylates containing acrylate urethane groups according to German Patent No. 1,230,778, polyacrylates containing butyl groups of the type described, for example, in U.S. Patent Nos. 3,124,005, 3,291,372 and 3,134,985 and in British Patent No. 888,008, polyacrylates produced by isomerization reactions of the type described for example in U.S. Patent No. 3,684,168, polyacrylates containing ester groups of the type described, for example, in British Patent Nos. 888,476 and 1,672,888, in U.S. Patent No. 3,687,763 and in German Patent No. 1,231,888, reaction products of the above-mentioned diacrylates with acrolein according to German Patent 1,672,368 and polyacrylates containing polymeric fatty acid esters according to U.S. Patent No. 3,468,883.

It is also possible to use diisocyanate monomers having isocyanate groups attached to the commercial production of isocyanates, optionally in solution in one or more of the above-mentioned polyacrylates. It is also possible to use any mixture of the above-mentioned polyacrylates.

Preferred polyacrylates are hexamethylene diacrylates, 1,6-hexamethylene diacrylates, 1-isocyanato-3,3,5-trimethyl-6-oxocyclohexenyl cyclohexane diacrylates, the toluene diacrylates and their isocyanates, the mixed isocyanates of toluene diacrylates and hexamethylene diacrylates, the reaction product of 1 mol of toluene diacrylate and 3 mols of toluene diisocyanate and also crude diphenyl methane diisocyanate.

Suitable compounds containing at least 2 isocyanate-reactive hydrogen atoms can be high or low molecular weight compounds, having a weight average molecular weight, generally from about 80 to 80,000. In addition to compounds containing amino groups, thiol groups or carbonyl groups, one, particularly compounds containing hydroxyl groups, particularly compounds containing from about 2 to 10 hydroxyl groups and above all, compounds having a weight average molecular weight of from about 200 to 2000, preferably from about 700 to 2000, for example, polyethers, polyesters, polyurethanes, polyacetals, polycarbonates, polyethersulfones, and polyester amides, containing at least 2, generally from about 2 to 8, but preferably from about 2 to 4 hydroxyl groups, or one hydroxyl-containing prepolymer of these compounds and a less than equivalent quantity of polyisocyanate of the type known for the production of polyurethanes.

Representatives of the above-mentioned compounds used in accordance with the present invention are described, for example, in High Polymers, Vol. VII, "Polyurethanes, Chemistry and Technology", by Saunders and Rush, Interscience Publishers, New York-London, and Vol. I, 1958, pages 28 to 48 and pages 49 to 66 and Vol. II, 1964, pages 6-9 and 149-163, and in "Kunststoffe-Handbuch", Vol. VI, Verlag VCH, Weinheim, Carl-Hanser-Verlag, Munich, 1969, for example on pages 48 to 71, 144, 145, it covers possible to use mixtures of the above-mentioned compounds containing at least two isocyanate-reactive hydrogen atoms and having a molecular weight of from about 80 to 80,000, for example, urethane polyesters and polyethers.

In some cases, it is particularly advantageous to combine low-melting and high-melting polyacrylates containing compounds with one another (German Offenlegungsschrift No. 2,768,887).

Low molecular weight compounds containing high but not very high-melting hydrogen atoms (molecular weight from about 80 to 400) suitable for use in accordance with the present invention are

EXAMPLE 1

Several organometallic compounds $[\text{CoFe}(\text{CO})_2]_2$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$ and $[\text{CoMo}(\text{CO})_9]_2$ were obtained from Pressure Chemical Company and used without further purification. The other compounds were prepared using standard organometallic synthetic techniques. The procedure used will be illustrated for the preparation of $[\text{CoFe}(\text{CO})_2]_2\text{SnPh}_3$.

The anion $[\text{CoFe}(\text{CO})_2]^-$ was produced by reducing 3.0 g of $[\text{CoFe}(\text{CO})_2]_2$ with 0.41 g of sodium and 10 ml of benzophenone in 200 ml of freshly distilled tetrahydrofuran under an atmosphere of argon. The solution was allowed to proceed for about 24 hours by which time the starting material had all been reduced to the anion as indicated by infrared spectroscopy (IR). To the solution of the anion was added 6.5 g of CSnPh_3 as a solid. The reaction was stirred until the anion was consumed as shown by IR. The reaction vessel was opened to air and the solvent removed under reduced pressure. The solid residue was taken up in methylene chloride and passed down a short silica gel column. Crystals were obtained by removing the methylene chloride under reduced pressure and adding heptane. The product was identified by IR, nuclear magnetic resonance spectroscopy (NMR), elemental analysis and melting point in a similar manner as the other materials in Table I were prepared.

These compounds are used in subsequent examples.

TABLE I

Characterization of Compounds				
Elemental Analysis (Report/Calculated)				
Compound	%C	%H	Melting Point, °C	
$[\text{CoFe}(\text{CO})_2]_2\text{SnPh}_3$	57.0/57.0	3.8/3.8	135-136	
$[\text{CoFe}(\text{CO})_2]_2\text{GaPh}_3$	62.3/62.4	4.2/4.2	159-160	
$[\text{CoFe}(\text{CO})_2]_2\text{PbPh}_3$	48.7/48.8	3.3/3.2	146-149	
$[\text{CoHf}(\text{CO})_2]_2\text{SnPh}_3$	51.0/50.7	2.8/2.8	142-149	
$[\text{CoHf}(\text{CO})_2]_2\text{MnPh}_3$	30.9/30.8	1.6/1.5	138-139	
$[\text{CoHf}(\text{CO})_2]_2\text{CoMoSnPh}_3$	52.6/52.5	3.4/3.4	213-214	

EXAMPLE 2

Several organometallic compounds were prepared according to literature methods. $[\text{CoW}(\text{CO})_9]_2\text{CH}_3$ was prepared according to the method of T. S. Piper, G. Wilkinson, *Inorg. Nucl. Chem.*, 1958, 3104-124. $[\text{CoW}(\text{CO})_9]_2$ was prepared according to the method of R. B. Nielsen, P. H. Nielsen, A. R. Manning, J. Organomet. Chem., 1978, 157-228. $[\text{CoFe}(\text{CO})_2]_2\text{SnPh}_3$ was prepared according to the method of G. Carver, E. Colomer, P. J. W. E. Douglas, J. Organomet. Chem., 1977, 135, 373, 388. The method of J. P. Biber, A. Worch, J. Amer. Chem. Soc., 1955, 77, 4882, was used to prepare $[\text{CoFe}(\text{CO})_2]_2(\text{CH}_3\text{Ph})_2$ and that of R. B. Nielsen, M. B. Nielsen, J. Organomet. Chem., 1984, 2, 15-37, to prepare $[\text{CoFe}(\text{CO})_2]_2(\text{COPh})_2$. The preparation of $[\text{CoFe}(\text{CO})_2]_2$ has been described in U.S. Patent No. 4,800,464. These compounds are used in subsequent examples.

EXAMPLE 3

This example illustrates the use of an organometallic compound containing a transition metal-transition metal single bond in the curing agent to photocatalyze the formation of polyurethane. A stock solution of 4,4'-methylenebis(cyclohexylisocyanates) (Desmodur W, a Mobay Corp., Pittsburgh, PA) and 1,4-bis(methylene glycol) in 400 (CarbowaxTM 400, Union Carbide, Danbury, CT) was prepared. To a solution of $[\text{CoFe}(\text{CO})_2]_2$ and 0.02 g Ph_3P , 0.1 g gamma-butyrolactone was added 1.25 g of

the stock solution. The sample was photocured to a solid using a KodakTM CarouselTM projector in 12 minutes.

Three samples were prepared as above, except the iron dimer and osmium salt were added as follows: sample (a), 0.01 g $[\text{CoFe}(\text{CO})_2]_2$, 0.03 g Ph_3P , PF_6^- ; sample (b), 0.01 g $[\text{CoFe}(\text{CO})_2]_2$, sample (c), 0.03 g Ph_3P , PF_6^- . (a) was left in the dark while samples (b) and (c) were irradiated as above. None of the three samples showed evidence of any curing, no obvious change in viscosity as evidence, after 20 minutes.

EXAMPLE 4

This example illustrates the use of an organometallic compound containing a transition metal-carbon single bond in the curing agent to photocatalyze the formation of polyurethane. 0.52 g Desmodur W (4,4'-methylene bis (cyclohexyl isocyanates)) and 0.72 g Carbowax 400 (polyol) were combined and added to 0.01 g $[\text{CoFe}(\text{CO})_2]_2$ (Cp = eta^5 -cyclopentadienyl) which had been dissolved in ca. 0.15 ml of a mixture of CH_2Cl_2 and gamma-butyrolactone. The resulting mixture was irradiated with a HanoviaTM 450 watt medium pressure mercury arc lamp through PyrexTM. Complete cure was achieved within 12 minutes irradiation time.

EXAMPLE 5

This example illustrates the photocuring of polyurethane precursors to polyurethanes in the presence and absence of O_2 using transition metal-transition metal bond containing organometallic compounds and osmium salt as curing agent.

A mixture of 10 mg $[\text{CoFe}(\text{CO})_2]_2$, 30 mg Ph_3P , PF_6^- , 0.1 g gamma-butyrolactone, 0.2 g DesmodurTM W (4,4'-methylenebis(cyclohexylisocyanates)), and 1.17 g polyethyleneglycol ($\text{MW} = 400$) was divided in half, one half was bubbled with N_2 for 2-3 minutes, the other left open to the atmosphere. Both samples were irradiated simultaneously with the output of a 450 watt Hanovia mercury arc, filtered through Pyrex and a water infrared filter. Both samples cured after 10.0 minutes irradiation. This demonstrates the presence of osmium salt curing occurs with or without O_2 present.

EXAMPLE 6

This example describes the photocuring of polyurethane precursors using transition metal-transition metal bond containing organometallic compounds and osmium and sulfonium salts. A stock solution was prepared from 7 Desmodur W, 1.9 parts butanediol, and 0.5 parts trimethylolpropane. Samples were prepared as in Example 3 using 1.25 g of the stock solution, 0.01 g neutral metal-metal bonded compound and 0.015 g Ph_3P , PF_6^- in 0.05 g gamma-butyrolactone. Irradiations were carried out on a 450 W Hanovia medium pressure mercury arc through Pyrex. Alternatively, these compositions can be cured thermally.

TABLE II

Organometallic compound	Cure time, minutes	
	Ph ₃ P ⁺ PF ₆ ⁻	Ph ₃ S ⁺ PF ₆ ⁻
[(Cp)Fe(CO) ₂] ₂	8.0	>100
[(Cp)Fe(CO) ₂] ₂	8.0	20-25
[(Cp)Fe(CO) ₂] ₂	12-20	7-12
[(Cp)Fe(CO) ₂] ₂	20-40	20-40
[(Cp)Fe(CO) ₂] ₂	40-65	55-65
[(Cp)Fe(CO) ₂] ₂	55-67	60-65
[(Cp)Fe(CO) ₂] ₂	about 60	—

EXAMPLE 7

This provides further examples of biscomponent curing agents wherein organometallic compounds contain transition metal-carbon bonds which are effective in the curing agent for polyurethane precursors. A stock solution of polyurethane precursor was prepared by mixing 23.1 g Desmodur W and 32.6 g Carbowax 400 and shaking well before use. Samples were prepared by dissolving 10 mg catalyst and 20 mg diphenyliodonium hexafluorophosphate (if used) in 0.2 g CH₂Cl₂. 2.0 g stock solution was added in the dark, and samples were then irradiated under a Hanovia Quartz Utility Lamp. The temperature of samples under the lamp reached ca. 50 °C within 10 min. The time to a viscosity increase is noted in Table III, and "cure time" is the time for a sample to become so viscous that it would not flow. "Partial cure" is indicated when, within 30 min irradiation, the sample became more viscous but would still flow.

TABLE III

Curing of Urethane Precursors	Cure Rates, min	
	Viscosity increase	Cured
CpPPh ₃	7	30
CpPPh ₃ + collman	7	30
CpPPh ₃ CO ₂ Me	30	partial
CpPPh ₃ CO ₂ Me + iodonium	30	partial
(PhMe) ₂ Ph ₂ PPh ₃ (hexafluoroantimonate) + PF ₆ ⁻	15	partial
[(Cp)Fe(CO) ₂] ₂ + iodonium ^a	9	30

^a included for purposes of comparison

The data show curing occurs with or without iodonium salts. In some cases, adventitious oxygen can provide a suitable oxidizing agent. However, the use of osmium salts is preferred since it is much easier to control the organometallic-oxidizing agent ratio.

EXAMPLE 8

This example describes the use of the curing agent containing an organometallic compound containing a transition metal-carbon bond to cure epoxies. Each sample was prepared by dissolving 10 mg catalyst and 20 mg diphenyliodonium hexafluorophosphate (if used) in 0.2 g CH₂Cl₂. 2.0 g cyclohexene oxide was added in the dark, and samples were then irradiated under a Hanovia Quartz Utility Lamp. Initial formation of polymer was tested by placing a few drops of the sample in about 2 ml methanol. Formation of precipitate indicated that polymer had formed. Further polymerization resulted in a viscosity increase in the samples. Results are indicated in Table IV.

TABLE IV

Curing Agent	Precipitate formed, mm	Viscosity increased min
CpPPh ₃	no cure	no cure
CpPPh ₃ + iodonium	3.5	30
CpPPh ₃ (CO ₂)Me + iodonium	3	30
(PhMe) ₂ Ph ₂ PPh ₃ (hexafluoroantimonate) + PF ₆ ⁻	2	no further cure
[(Cp)Fe(CO) ₂] ₂ + iodonium	2	30

^a included for purposes of comparison.

EXAMPLE 9

Examples of the ability of curing agent containing transition metal-transition metal bonded and (M-L) type organometallic compounds and osmium salt to photoinduce the cure of epoxies are provided here. The tests were carried out in the following manner: into a glass vial were weighed out 0.10g of the desired organometallic compound and/or 0.20g diphenyliodonium hexafluorophosphate (3M Company, recrystallized from acetone/isopropanol). Then, the following operations were carried out under subdued light. 0.3g of gamma-butyrolactone, 2.0g cyclohexene oxide (Aldrich Chemical Company, distilled), 5.0g of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexene carboxylate (EPR-4271, Union Carbide Company) were added to prepare the coating solution. The solutions were coated onto 78 micrometers (3 mil) polyethylene chloride subbed polyester (3M Company) using a #22 wire wound rod. The sample coatings were exposed, in air, to a 275 watt G.E. sunlamp at a distance of 10cm. The time to "set to color" is recorded in Table V. That is the time needed to cure the coating so that when it is touched with a cotton ball, it leaves no smudges or picks up no cotton threads. This test establishes the time required to cure the coating. Under conditions of this test, the diphenyliodonium hexafluorophosphate alone requires greater than 10 min to cure.

TABLE V

Compound	Cure Time ^a	
	No Onium Salt Added	Onium Salt Added
[CpFe(CO) ₂] ₂	>10	1
CpFe(CO) ₂ SnPh ₃	>10	5
CpFe(CO) ₂ GePh ₃	>10	5
[CpFe(CO) ₂] ₂ SnPh ₃	>10	3
Me ₂ (CO) ₂	>10	1
(CO) ₂ MeSnPh ₃	>10	4
(CO) ₂ Me ₂ SnPh ₃	1	3
Re ₂ (CO) ₉	8	1.5
CpFe(CO) ₂ SnPh ₃		4

a time in minutes to cure.

EXAMPLE 10

To further demonstrate the activity of the curing agent, a series of experiments were carried out in another epoxy and/or acrylic composition. The organometallic compound, with and without the onium salt, was photolyzed in presence of an epoxy or acrylic. The specific system used is as follows: methyl acrylate was distilled from hydroquinone and stored cold until ready for use. Cyclohexane oxide was used as obtained from Aldrich. The organometallic compounds were obtained from commercial sources. Diphenyliodonium hexafluorophosphate was recrystallized from acetone-isopropanol. All experiments were done at 100% solids, except as noted.

In a small vial was placed 0.02 g of the organometallic compound with/without 0.04 g of the iodonium salt along with 2 g of the desired monomer. For the acrylic tests, the solutions were purged with N₂ for 60 sec before and continuously during the photolysis. The epoxy tests were performed without purging, vents to the air. The light source was one 15 watt daylight fluorescent bulb. In Table VI below, the cure times represent the time required to reach the same degree of cure, usually gelation of the solution. Alternatively, the compositions can be cured thermally.

TABLE VI

Photoinitiated Cure Times of Epoxy and Acrylic Compositions ^a	
Catalyst System	Expiry Acrylics
[CpFe(CO) ₂] ₂	>600
[CpFe(CO) ₂] ₂ Iodonium	60
Me ₂ (CO) ₂	>600
Me ₂ (CO) ₂ Iodonium	40
Re ₂ (CO) ₉	>600
Re ₂ (CO) ₉ Iodonium	200
Co ₂ (CO) ₈	200
Co ₂ (CO) ₈ Iodonium	b
Cu ₂ (CO) ₉	c
Cu ₂ (CO) ₉ Iodonium	d
Cu ₂ (CO) ₉ Acetone ^d	>600
Iodonium	>300

a Cure time in seconds.

b Not done.

c Reacted in the dark upon mixing.

d 10% by wt. gamma-butyrolactone added.

EXAMPLE 11

This example demonstrates the ability of transition metal-halogen metal bonded and M-L type organometallic compounds to photoinitiate the cure of ethylenically-unsaturated compounds in the presence of iodonium salts. The tests were carried out in the following manner: Into a glass vial were weighed out 0.05g of the desired organometallic compound and/or 0.10g diphenyliodonium hexafluorophosphate (DM Company, recrystallized from acetone-isopropanol). Then, the following operations were carried out under subdued light: 0.2g of gamma-butyrolactone, 5.0g methyl acrylate (Aldrich Chemical Company, distilled from hydroquinone), 5.0g of perfluorinated tetraerythritol (PF-255, Sarnes Company) were added to prepare the coating solution. The solutions were casted onto 75 micrometers (3 mil) polyethylene chloride subbed polyester (3M Company) using a #22 wire wound rod. The sample coatings were casted with a second sheet of polyester and exposed to two 15 watt Sylvania blacklight bulbs at a distance of 2 cm. The time required to produce a tacky cured coating was recorded. Under the conditions of this test, the diphenyliodonium hexafluorophosphate alone requires greater than 15 min to cure.

TABLE VI

Curing of Ethylenically Unsaturated Monomers		
Organometallic Compound	Cure Time ^a	
	No Orum Salt Added	Orum Salt Added
[CpFe(CO) ₂] ₂	>800	15
CpFe(CO) ₂ SnPh ₃	>800	120
CpFe(CO) ₂ GePh ₃	>800	120
[CpFe(CO) ₂] ₂ SnPh ₃	>800	60
Mn ₂ (CO) ₁₀	>800	<15
(CO) ₅ MnSnPh ₃	300	300
(CO) ₅ Mn ₂ SnPh ₃	60	30
Re ₂ (CO) ₉	120	60
[CpFe(CO) ₂] ₂ ^b	>800	30
CpFe(CO) ₂ SnPh ₃	>800	240

^a time in seconds to cure.
^b saturated solution, <0.01g dissolved.

EXAMPLE 12

Further examples of the curing of ethylenically unsaturated monomer (25 g of pentaerythritol triacrylate in 225g acetone) or epoxy monomer (cyclohexene oxide) are provided here. A curable composition consisted of 0.01g of the organometallic compound or 0.02g of diphenyliodonium hexafluorophosphate or these same amounts of both compounds added to either r-normer. The light sources used were for UV exposure, about 380 nm, two 15 watt G.E. blacklight bulbs and/or the visible, a Kodak Carousel Projector or the projector with a 440 nm filter. The initiation of polymerization was detected by solution gelation for the acrylate and for the epoxy the precipitation of the polymer from a 2% ammoniumsulfate solution. Free radical systems were purged with N₂ for 2 minutes before and continuously during irradiation while the carbonyl samples were left open to the air without purging. Sample size was 2 to 3 mL in a 13 x 100 mm pyrex test tube. The results of these tests are shown in Table VIII.

TABLE VII

Photoreacted Cure Times of Epoxy and Acrylate Compositions ^a		
Curing Agent	Epoxy	Acrylate
[CpFe(CO) ₂] ₂	>1000 90°	>1000 >5°
[CpFe(CO) ₂] ₂ -iodonium ^c	90° >100°	<5° >300°
Mn ₂ (CO) ₁₀	>1000 >100°	>1000 <10°
Mn ₂ (CO) ₁₀ -iodonium ^c	>100°	<10°

^a Cure times given in seconds.

^b Unfiltered projector as light source.

^c The diphenyliodonium salt showed no indication of polymerization by itself under these same conditions.

^d 440 nm filter used with the projector.

^e Blacklight used as the light source, ca 380 nm.

EXAMPLE 13

Examples of the photocuring of ethylenically unsaturated monomers using transition metal-transition metal bond containing organometallic compounds and iodonium salts are given here.

Samples were prepared as 1.0 g methyl acrylate containing 0.01 g metal-metal bond containing complex and 0.015 g Ph₄⁺ PF₆⁻. Up to 0.05 g butadiene or methylene chloride were used to dissolve the photocatalyst systems. Samples were bubbled with N₂ and irradiated using a Kodak Carousel slide projector, with a 380 nm cutoff filter, and the time required to cure the sample recorded in Table IX. Alternatively, the compositions can be cured thermally.

TABLE IX

Curing of Ethylenically Unsaturated Monomers		
Compound and Ph ₄ ⁺ PF ₆ ⁻	Conditions	Cure Time
[CpFe(CO) ₂] ₂	irrad.	30 sec, slow dark reaction
Mn ₂ (CO) ₁₀	irrad.	30 sec, no dark reaction
[CpFe(CO) ₂] ₂	irrad.	40 sec, no dark reaction
[Re(CO) ₅] ₂	irrad.	8 min, no dark reaction
Co ₂ (CO) ₈	irrad.	minutes, slow dark reaction
Co ₂ (CO) ₈	Dark	Cures during desorption

EXAMPLE 14

This example describes the curing of ethylenically-unsaturated monomers with transition metal-transition metal bond containing organometallic compounds. Each sample was prepared by dissolving 10 mg catalyst and 20 mg

When the curing agent was added in 0.2 g gamma-butyrolactone, 2.0 g methyl acrylate was added to remove inhibitors) was added in the dark and nitrogen was bubbled through the sample for 2 min to remove oxygen. Samples were then irradiated in front of a Kodak Carousel Projector containing a 300 nm cutoff filter. If no curing occurred in 15 min, the sample was then irradiated for 15 min under a Quartz Halogen lamp. In Table X, "cure time" refers to the time required for a sample to solidify. Alternatively, these examples can be cured thermally.

TABLE X

Curing of Vinyl Ethylenically-Unsaturated Monomer	
Curing Agent	Cure time, min
CpPh ₃	15 (Norton)
CpPh ₃ + Iodonium	6 (Kodak)
CpW(CO) ₂ Me	no cure
CpW(CO) ₂ Me + Iodonium	3.5
[CpFe(CO) ₂] ₂ + Iodonium ^a	0.5 (dark cure)

^a Included for purposes of comparison

EXAMPLE 15

This example describes the use of [CpW(CO)₂]₂ to cure polyurethane precursors, epoxies or ethylenically unsaturated monomers. Each sample contained 0.01 g [CpW(CO)₂]₂ and 0.02 g diphenylodonium hexafluorophosphate (if used) in 0.25 g gamma-butyrolactone, to which was added 2.0 g of precursor or monomer in a vial. Irradiation was then performed with a Kodak Carousel Projector (8 inches away), modified with a 300 nm filter. With a urethane precursor stock solution (prepared as in Example 4), in the presence or absence of onium salt, partial curing to produce a clear solution, occurred in 2 hour irradiation time. Upon standing in room light for 24 hours, an increase in viscosity occurred.

When cyclohexanone was used, and the curing agent consisted of [CpW(CO)₂]₂ onium an salt, vigorous, exothermic curing occurred within 3 min of irradiation.

When methyl acrylate was used as monomer, no curing occurred in the absence of onium salt. With onium salt present, the sample became viscous within 4 min and solid within 8 min of irradiation time.

Alternatively, the compositions can be cured thermally.

EXAMPLE 16

To demonstrate the utility of the curing agent for curing of polyurethane precursors, epoxies and vinyl monomers for the case where the organometallic compound contains a single bond between a transition metal and a Group IV element, the following samples were prepared. In a vial, 0.01 g of organometallic compound, 0.02 g of diphenylodonium hexafluorophosphate (if used, as indicated below), and 0.25 g of gamma-butyrolactone were gently agitated until dissolution of the organometallic compound was complete. 2.0 g of polyurethane precursor or monomer was added in reduced light, the vial was capped, and the sample irradiated in front of a Kodak Carousel projector fitted with a 300 nm cutoff filter at a distance of nine inches, and at room temperature (about 25 °C). Particular details and any experimental variations are indicated in Table XI.

TABLE XI

Cure Times: Photoinitiated Curing of Polyurethane Precursors, Epoxies and Vinyl Monomers with Transition Metal

Group IVA Compounds

Curing agent	Urethane ^a	Epoxies ^b	Vinyl ^c
[CpFe(CO) ₂] ₂	120 min (VV) ^e	2	no cure
[CpFe(CO) ₂] ₂ /Iodonium ^d	60 min (VV)	30 sec	1.8 min
CpFe(CO) ₂ (CH ₂ Ph)	40 min (V)	2	no cure
CpFe(CO) ₂ (CH ₂ Ph)/Iodonium	40 min (V)	12 min	23 min
CpFe(CO) ₂ (COPh)	120 min (V) ^e	2	no cure
CpFe(CO) ₂ (COPh)/Iodonium	120 min (V) ^e	5 min	48 hr ^g
CpFe(CO) ₂ (SiPh ₃)	45 min (V) ^h	2	no cure
CpFe(CO) ₂ (SiPh ₃)/Iodonium	45 min (V) ^h	5 min	48 hr ^g
CpFe(CO) ₂ (GePh ₃)	36 min (V) ^h	2	no cure
CpFe(CO) ₂ (GePh ₃)/Iodonium	36 min (V) ^h	2.75 min	no cure
CpFe(CO) ₂ (SnPh ₃)	36 min (S) ^h	2	no cure
CpFe(CO) ₂ (SnPh ₃)/Iodonium	36 min (V) ^h	2 min	no cure
CpFe(CO) ₂ (PbPh ₃)	45 min (S) ^h	2	no cure
CpFe(CO) ₂ (PbPh ₃)/Iodonium	33 min (VV) ^h	no cur	no cure

- a. Polyurethane precursors are from a stock solution consisting of 23.1 g of DesmodurTM W and 32.6 g of Carbowax 400. Cure times are followed by an indication in parentheses of extent of cure, where V = viscous, VV = very viscous, S = solid.
- b. Monomer is cyclohexene oxide, purified by distillation. Cure time is defined as the time necessary to observe formation of precipitate when one drop of sample is placed in 2 mL of methanol.
- c. Monomer is methyl acrylate, purified prior to use by distillation under reduced pressure. After monomer addition but before irradiation, samples were deoxygenated by bubbling a stream of nitrogen gas through the solution for 2 min, with care being taken to prevent any light from reaching the sample during oxygenation. Cure is defined by an increase in solution viscosity or a sudden exotherm indicating rapid polymerization (also accompanied by a sudden increase in viscosity).
- d. Included for purposes of comparison to data in other Tables.
- e. 60 min irradiation with Carousel Projector, followed by 60 minutes of irradiation in room (fluorescent) light.
- f. This particular combination was not tested.
- g. 30 minutes irradiation with Kodak projector, following by 30 minutes irradiation under a Hanovia Quarts Utility Lamp (6 inches from bulb), followed by sample storage/irradiation in room (fluorescent) light.
- h. Irradiation with Hanovia Quarts Utility Lamp (15 cm from bulb) in place of the Kodak Projector.

EXAMPLE 17 (comparative)

This example illustrates the dual curing of polyurethane precursors and ethylenically-unsaturated monomers using the curing agent $[\text{CpFe}(\text{CO})_2]_2\text{PhI}$ PF₆.

Samples 1-25 g in size, were prepared from stock solutions of 2.08 parts DesmodurTM W (4,4'-methylenebis(cyclohexylisocyanate)), 2.08 parts polyhexamethylene glycol (MW = 400), 9.0 parts methyl acrylate (freshly distilled), and 0.06 parts $[\text{CpFe}(\text{CO})_2]_2$. To half of this stock solution was added 0.002 parts PhI.

PF₆⁻. Molar ratios for sodium salt/iron dimer = 2:1, $\text{NCO}/\text{OH} = 1.0$, weight % iron dimer = 0.9%, sodium salt = 1.2%. Samples were irradiated simultaneously using 300 nm Sn^{2+} tube (15 watts) for 10 min, then analyzed by 400 MHz ¹H nuclear magnetic resonance spectroscopy. Conversions are listed in Table XI.

TABLE XI

Dual Curing of Polyurethane Precursors and Ethylenically-Unsaturated Monomers			
Oxium Salt	Conditions	Conversion to Polymer	
PhI	Dark	Acrylate	Urethane
PhI	irradiation	70%	50%
PhI	irradiation, deoxygenated	70%	8%
None	dark	0%	11%
None	irradiation	24%	70%
None	irradiation, deoxygenated	100%	10%

EXAMPLE 18 (comparative)

This example demonstrates simultaneous curing of ethylenically unsaturated monomers and epoxies. Gelation times will not show that both monomers have reacted at the same time. It is possible to use nuclear magnetic resonance spectroscopy to differentiate the two polymers in the presence of each other. The experiment was carried out in the following manner: A 1/1, v/v, mixture of methyl acrylate-cyclohexene oxide was prepared. To a 10g sample of this mixture was added 0.04g of $[\text{CpFe}(\text{CO})_2]_2$ or $\text{Me}_4\text{Fe}(\text{CO})_5$ or diphenylchloronium hexafluorophosphate (0.034g with the monomer 0.03 g with the monomer dimer) or the specified amounts of both compounds. In a small vial was placed 2 mL of the sample and it was purged for 1 min before and continuously during irradiation. The light source was two 15 watt G.E. incandescent bulbs. Irradiation time was 2 minutes. Immediately after completion of the polymerization, the NMR in CDCl_3 was taken. The amount of polymerization was determined by the ratio of the peak intensity of the polymer to that of polymer plus monomer. The results of the study are shown in Table XII.

TABLE XII

Percent Conversion to Polymer from NMR Study ^a			
Curing Agent	Epoxies	Acrylates	
$[\text{CpFe}(\text{CO})_2]_2$	0 ^b	15	
$[\text{CpFe}(\text{CO})_2]_2$ -monomer	35	60	
iodonium	<1	<10	
$\text{Me}_4\text{Fe}(\text{CO})_5$	<0.5	<0.5	
$\text{Me}_4\text{Fe}(\text{CO})_5$ -monomer	37	47	

a. NMR's taken by on a 400 MHz instrument.
b. None detected in the NMR.

As can be seen from the NMR results, the system efficiently reacted both epoxy and less reactive polymerization simultaneously.

EXAMPLE 19 (comparative)

This example demonstrates the simultaneous curing of ethylenically unsaturated and epoxy monomers in a simultaneous system. The curable composition consists of methyl acrylate, cyclohexene oxide and diglycidyl ether of tetraethylene glycol. Only if both epoxy and acrylate cure are initiated will a crosslinked insoluble polymer be obtained.

All monomers were distilled before use; methyl acrylate and glycidyl acrylate from hydroquinone. Sample preparations were carried out under subdued lights. The polymerizable mixture consisted of 0.2 g gamma-butyrolactone, 1.0 g glycidyl acrylate, 5.0 g methyl acrylate and 5.0 g cyclohexene oxide. Depending on the test added to this were 0.05 g of the desired organometallic compound and/or 0.1 g dichlorodioxane hexafluorophosphate. A 3 g portion of this composition was placed in a glass vial and irradiated between two 15 watt G.E. daylight fluorescent tubes using an Ultraviolet Products lamp holder (lamp separation distance 4 cm). The sample was purged with nitrogen for one minute preceding and continuously during photolysis. The irradiation time required to produce a polymer insoluble in chloroform was recorded and is noted in Table XIV.

Alternatively these compositions can be cured thermally.

TABLE XIV

Compound	Simultaneous Photoinitiation of Free Radical and Epoxy Cure in a Crosslinkable System	
	No Onium Salt Added	Onium Salt Added
$[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$	> 15	1
$\text{Cp}^*\text{Fe}(\text{CO})_2\text{SnPh}_3$	> 15	10
$\text{Cp}^*\text{Fe}(\text{CO})_2\text{GaPh}_3$	> 15	15
$[\text{Cp}^*\text{Fe}(\text{CO})_2]_2\text{SnPh}_3$	> 15	10
$\text{Me}_2\text{C}(\text{CH}_3)_2$	> 15	15
$(\text{C}_6\text{H}_5)_3\text{MnSnPh}_3$	> 15	10
$(\text{CO})_2\text{Mn}(\text{Ph})_2\text{SnPh}_3$	> 10	4
$\text{Re}_2(\text{CO})_{10}$	> 10	5
$[\text{Cp}^*\text{Ir}(\text{CO})_2]_2$	> 15	15
$\text{Cp}^*\text{Ir}(\text{CO})_2\text{SnPh}_3$	> 15	10

a time in minutes to produce insoluble crosslinked system.
Diphenyliodonium hexafluorophosphate alone under these conditions did not produce a crosslinked system after 15 minutes.

b Only 0.01g of the compound was used.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of the invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

Claims

1. A polymerizable composition comprising one class of polymeric precursors selected from the group consisting of 1) at least one ethylenically-unsaturated monomer, 2) at least one epoxy monomer, and 3) polyurethane precursors, and a curing agent comprising an organometallic compound and an onium salt, and a solvent.
2. The composition according to claim 1 which is photopolymerizable.

3. The composition according to claim 1 wherein said class of polymeric precursors is at least one ethylenically-unsaturated monomer or polyurethane precursor and said composition is thermally polymerizable.
4. The composition according to claims 1 to 3 wherein said organometallic compound has the formula:



wherein

- L₁ represents none, or 1 to 12 ligands contributing p-electrons that can be the same or different ligands selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing 2 to 24 p-electrons to the valence shell of M;
- L₂ represents none, or 1 to 24 ligands that can be the same or different contributing an even number of p-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M;
- L₃ represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron to the valence shell of each M;
- Ligands L₁, L₂, and L₃ can be bridging or non-bridging ligands;
- M represents 1 to 4 of the same or different metal atom selected from the elements of Periodic Groups IVB, VB, VIB, VII, VIII, and VIII; with the proviso that said organometallic compound contains at least one of a metal-metal sigma bond and L₁ and with the proviso that L₁, L₂, L₃ and M are chosen so as to achieve a stable configuration.

5. The composition according to claims 1 to 4 wherein said onium salt has the formula II



wherein A is an iodonium, sulfonium, or dication cation, and

- X is an organic sulfonate counterion, or a halogenated metal or metalloid counterion.
6. The composition according to claims 1 to 5 wherein said ethylenically-unsaturated monomer is selected from the group consisting of acrylates, acrylamides and vinyl compounds.
7. The composition according to claims 1 to 5 wherein said polyurethane precursors comprise a mixture of polyisocyanates and compounds bearing at least two isocyanate-reactive hydrogen atoms where the ratio of isocyanate groups to isocyanate-reactive hydrogen atoms is in the range 1:2 to 2:1.
8. A process comprising the steps of:
 - a) providing a polymerizable composition according to claims 1 to 7, and
 - b) allowing said mixture to polymerize or adding energy to said mixture to effect polymerization.
9. A layered structure comprising a substrate having coated on one surface thereof the polymerizable composition according to claims 1 to 7.
10. The layered structure according to claim 9 which is an imposable structure.
11. The polymerizable composition according to claims 1 to 7 and 9 which has been cured.
12. A shaped article according to claim 11.